"Designer" Biodiesel: Optimizing Fatty Ester Composition to Improve Fuel Properties[†]

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Biodiesel is a domestic and renewable alternative with the potential to replace some of the petrodiesel market. It is obtained from vegetable oils, animal fats, or other sources with a significant content of triacylglycerols by means of a transesterification reaction. The fatty acid profile of biodiesel thus corresponds to that of the parent oil or fat and is a major factor influencing fuel properties. Besides being renewable and of domestic origin, advantages of biodiesel compared to petrodiesel include biodegradability, higher flash point, reduction of most regulated exhaust emissions, miscibility in all ratios with petrodiesel, compatibility with the existing fuel distribution infrastructure, and inherent lubricity. Technical problems with biodiesel include oxidative stability, cold flow, and increased NO_x exhaust emissions. Solutions to one of these problems often entail increasing the problematic behavior of another property and have included the use of additives or modifying the fatty acid composition, either through physical processes, such as winterization, or through genetic modification. Methyl oleate has been proposed as a suitable major component of biodiesel in this connection. In this work, the properties of various potential major components of biodiesel are examined and compared. For example, while methyl oleate has been suggested as such a major component, methyl palmitoleate has advantages compared to methyl oleate, especially with regards to low-temperature properties. Other materials that are examined in this connection are short-chain (C_8–C_{10}) saturated esters, with only C_{10} esters appearing suitable. It is also suggested that to obtain biodiesel fuel with favorable properties, it is advantageous for the fuel to consist of only one major component in as high a concentration as possible; however, mixtures of components with advantageous properties as described here may also be acceptable.

Introduction

The replacement of fossil fuels to secure future energy supplies continues to be a major concern. In this connection, biodiesel[1,2] is an alternative to petroleum-based diesel fuel (petrodiesel). A reaction commonly referred to as transesterification yields biodiesel from vegetable oils or other materials largely comprised of triacylglycerols, such as animal fats or used frying oils, and monohydric alcohols. The resulting monoalkyl esters possess fuel and physical properties that are competitive with petrodiesel. The fatty acid profile of biodiesel is identical to that of the parent oil or fat. Advantages of biodiesel include domestic origin, renewability, biodegradability, higher flash point, inherent lubricity, reduction of most regulated exhaust emissions, as well as miscibility with petrodiesel. An essential feature of biodiesel is that its fatty acid composition corresponds to that of its parent oil or fat. Thus, biodiesel fuels derived from different sources can have significantly varying fatty acid profiles and properties.

Various specifications that a biodiesel fuel must meet are contained in biodiesel standards, such as American Society for Testing and Materials (ASTM) D6751 and EN 14214 in Europe. While many of these specifications are related to fuel quality issues, such as completeness of the transesterification reaction or storage conditions, several parameters directly depend upon the fatty acid composition of the biodiesel fuel. Among these specifications are cetane number, kinematic viscosity, oxidative stability, and cold-flow properties in form of the cloud point or cold-filter plugging point. Other important issues to consider that are influenced by fatty ester composition but are not contained in biodiesel standards are exhaust emissions, lubricity, and heat of combustion.

The most common fatty esters contained in biodiesel are those of palmitic (hexadecanoic) acid, stearic (octadecanoic) acid, oleic (9(Z)-octadecenoic) acid, linoleic (9(Z),12(Z)-octadecadienoic) acid, and linolenic (9(Z),12(Z),15(Z)-octadecatrienoic) acid. This holds for biodiesel feedstocks, such as soybean, sunflower, rapeseed (as canola), palm, and peanut oils. Some tropical oils, such as coconut oil, contain significant amounts of shorter chain acids, such as lauric (dodecanoic) acid. A variety of other fatty acids are found in minor amounts in virtually all oils and fats used as biodiesel feedstocks.

Technical problems with biodiesel that have persisted to the present are oxidative stability, poor low-temperature properties, and a slight increase in NO_x exhaust emissions, although the latter problem may fade over time with the advent of new exhaust emission control technologies. Solving these problems simultaneously has proven difficult because the solution to one of the problems often aggravates another problem. This behavior can be largely traced to the dependence of fuel properties on

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(1) *The Biodiesel Handbook*; Knothe, G., Krahl, J., Van Gerpen, J., Eds.; AOCS Press: Champaign, IL, 2005.
(2) Mittelbach, M.; Remschmidt, C. *Biodiesel—The Comprehensive Handbook*; M. Mittelbach: Graz, Austria, 2004.

the fatty acid structure.[3] Thus, it has been shown that the cetane number, a dimensionless descriptor related to the ignition quality of a diesel fuel, decreases with a decreasing chain length, an increased branching, and an increasing unsaturation in the fatty acid chain.[4] Generally, the higher the cetane number, the better the ignition quality. On the other hand, saturated esters, which have high and thus advantageous, cetane numbers, possess poor cold-flow properties. Unsaturated, especially polyunsaturated, fatty esters have lower melting points, which are desirable for improved low-temperature properties but also have low cetane numbers and reduced oxidative stability, which is undesirable for a diesel fuel.

Several approaches are possible to solve these problems. A common approach is the use of additives, such as antioxidants, cetane enhancers, or cold-flow improvers. This approach, however, raises the questions of additive compatibility, required additization levels, the effect on other properties, and if these additives function as designed for biodiesel fuels with differing fatty acid profiles. An approach toward improving low-temperature properties is winterization,[5,6] in which higher melting saturated esters are removed by repeated cooling cycles. This approach presents problems in terms of reduced oxidative stability and lower cetane numbers of the winterized material. A third approach is the production and use of esters other than methyl.[3,7] Thus, ethyl and *iso*-propyl esters have improved low-temperature properties[8] without comprising cetane number or oxidative stability. Problems with this approach are the significantly higher cost of the alcohols as well as changes required for the transesterification process. A fourth approach is the use of oils with inherently modified fatty acid profile (by genetic modification or other processes) giving advantageous fuel properties. Thus, methyl oleate has been suggested and studied as a prime component of such modified biodiesel fuels.[9,10] This approach, similar to the use of esters other than methyl, would simultaneously address the technical problems associated with biodiesel use without comprising other properties. Potential problems with this approach include reservations toward genetic modification as well as suitability of the modified oils for other purposes, especially nutrition.

Recently, a brief and preliminary discussion of some aspects of modifying the fatty ester composition of biodiesel was presented.[11] The present work investigates and expands this approach by compiling, determining, and evaluating relevant properties of fatty esters. Alternatives to methyl oleate, including esters of palmitoleic acid, saturated short-chain esters, hydroxy-containing esters, and esters other than methyl, are discussed.

Experimental Section

All fatty esters were purchased from Nu-Chek Prep (Elysian, MN) and were of >99% purity (no additives influencing oxidative stability, etc.) as verified by random checks using gas chromatography–mass spectrometry (GC–MS).

Melting points of low-melting fatty esters were determined using the heating scan starting at −90 °C of a differential scanning calorimeter (Model Q1000; TA Instruments, New Castle, DE) using American Oil Chemists' Society (AOCS) official method Cj 1-94. Melting points of some esters of lauric, palmitic, stearic, oleic, linoleic, and linolenic acids were available from the literature[12,13] for the sake of comparison. Also, for the sake of verification and comparison, the values for methyl laurate and methyl oleate were determined here and agreed excellently with literature values.

Additional kinematic viscosity data (for C_8 and some ethyl esters) were determined using the standard method ASTM D445. Other kinematic viscosity data were determined previously using the same method.[14,15]

Cetane numbers were determined at Southwest Research Institute, San Antonio, TX, with an Ignition Quality Tester (IQT) using the method ASTM D6890 as described previously.[16] Other cetane number data were obtained from literature compilations.[1] Relevant exhaust emission tests were conducted previously.[17]

Oxidative stability was determined with an oxidative stability instrument (OSI; AOCS method Cd 12b-92) or a Rancimat apparatus (Metrohm Instruments/Brinkmann Instruments, Westbury, NY; European standard EN 14112 for this method).

Results and Discussion

Various fatty esters were investigated for fuel properties contained in the biodiesel standards ASTM D6751 and EN 14214. These properties are cetane number, cold flow, kinematic viscosity, and oxidation stability, which are critical for the operation of a fuel in a diesel engine. Because neat compounds were studied here and cold flow is a "soft" specification in these standards, a "report to customer" being required in ASTM D6751 and EN 14214 using limits depending upon the location and time of year, the melting point was used as a cold-flow parameter.

Table 1 lists the specifications from ASTM D6751 and EN 14214 mentioned above. Table 2 contains the fatty acid profiles of some vegetable oils commonly used as biodiesel feedstock. Table 3 gives the fuel properties of some biodiesel fuels derived from these feedstocks. Table 4 presents the data of neat esters investigated here and in previous literature related to combustion and emissions. Additionally, in Table 5, the melting points, kinematic viscosity data at 40, 0, and −10 °C, as well as oxidative stability values of neat esters are given.

Beyond these properties contained in standards, exhaust emissions, heat of combustion, and lubricity will be discussed.

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Table 1. Specifications in Biodiesel Standards That Are Directly Influenced by the Fatty Acid Profile of the Biodiesel Fuel

specification	ASTM D6751	EN 14214
cetane number	47 minimum	51 minimum
kinematic viscosity at 40 °C (mm²/s)	1.9–6.0	3.5–5.0
cloud point	report	
cold-filter plugging point		not specified; depends upon the location and time of year
oxidative stability at 110 °C (h); Rancimat test	3 minimum	6 minimum

Table 2. Fatty Acid Profiles of Some Common Vegetable Oils Used or Suggested as Biodiesel Feedstocks[a]

vegetable oil	C16:0[b]	C18:0[b]	C18:1[b]	C18:2[b]	C18:3[b]	other
castor[c]	1	1	3	4		C18:1, 12-OH
coconut	7.5–10.5	1–3.5	5–8	1–2.6		C8:0, 4.6–10.0; C10:0, 5.0–10.0; C12:0, 44–53%; C14:0, 13–20.6%
cottonseed	22–26	2–3	15–22	47–58		
palm	40–47	3–6	36–44	6–12		
peanut	6–14	2–6	36.4–67.1	13–43		
rapeseed (canola)[b]	2–6	4–6	52–65	18–25	10–11	
soybean	10–12	3–5	18–26	49–57	6–9	
sunflower	5–7	3–6	14–40	48–74		

[a] Data are from refs 1 and 13. [b] C16:0, palmitic (hexadecanoic) acid; C18:0, stearic (octadecanoic) acid; C18:1, oleic (9(Z)-octadecenoic) acid; C18:2, linoleic (9(Z),12(Z)-octadecenoic) acid; and C18:3, linolenic (9(Z),12(Z),15(Z)-octadecenoic) acid. [c] Castor oil contains approximately 90% ricinoleic acid (12-hydroxy-9(Z)-octadecenoic acid) and also contains 9,10-dihydroxystearic acid.

Table 3. Fuel Properties of Biodiesel Fuels (Methyl or Ethyl Esters) from Various Sources[a]

vegetable oil	cetane number	heat of combustion (kJ/kg)	cloud point or CFPP (°C)	kinematic viscosity (40 °C; mm²/s)
coconut ethyl	67.4	38 158	5	3.08
cottonseed	51.2		−4 (PP)	6.8 (21 °C)
palm ethyl	56.2	39 070	8	4.5 (37.8 °C)
rapeseed (canola)[b]	48–56	37 300–39 870	−3; CFPP −6	4.53
soybean	48–56	39 720–40 080	from −2 to 3	4.0–4.3
sunflower	54–58	38 100–38 472	0–1.5	4.39

[a] Ranges are given when multiple values are given in the literature to reflect these values. All values in this table are compiled from ref 1. [b] High oleic rapeseed oil (canola oil).

Table 4. Properties of Fatty Esters Related to Combustion and Emissions

ester	cetane number[b]	heat of combustion (kJ/mol; kJ/kg)[c]	exhaust emissions relative to petrodiesel base fuel[a]			
			NO$_x$	PM	HC	CO
methyl octanoate	39.75 (0.57)	5523.76/34 907				
ethyl octanoate	42.19 (0.45)	6129.56/35 582				
methyl decanoate	51.63 (0.80)	6832.24/36 674				
ethyl decanoate	54.55 (0.95)	7447.52/37 178				
methyl laurate	66.70 (1.49)	8138.42/37 968	−5.0	−83.2	13.2	−28.8
methyl myristoleate	nd	9238.27/38 431				
methyl palmitate	85.9 (2.34)	10 669.20/39 449	−4.3	−81.9	−29.2	−43.1
methyl palmitoleate	56.59 (1.52); 51.0 (1.21)[d]	10 547.86/39 293				
methyl stearate	101 (3.35)	11 962.06/40 099				
methyl oleate	56.55 (1.52); 59.3 (1.30)[d]	11 887.13/40 092	6.2[e]	−72.9[e]	−54.6[e]	−49.0[e]
ethyl oleate	nd	12 525.17/40 336				
methyl ricinoleate	37.38 (1.55)					
methyl linoleate	38.2 (0.85)	11 690.10/39 698				
methyl linolenate[f]	22.7[d]	11 506.00/39 342				

[a] For details and characterization of the fuels used for determining these values, see ref 17. NO$_x$, nitrogen oxides; PM, particulate matter; HC, hydrocarbons; and CO, carbon monoxide. [b] Cetane numbers are derived cetane numbers as given in ref 16 or were determined additionally in the course of this work by the same method (ASTM D6890) as in ref 16. Standard deviations given in parentheses. [c] Heats of combustion are calculated from the heat of formation data in ref 12 using the equation given on p 5-89 in ref 12 or from experimental values (kg cal/mol) given in ref 21. [d] Cetane numbers of methyl palmitoleate and methyl oleate are determined in ref 16 and during the course of this work for the sake of comparison and repeatability. [e] Technical-grade methyl oleate (approximately 77%) is used. For details, see ref 17. [f] Cetane number for methyl linolenate is from references in ref 1.

Specifications in standards related to production, for example, glycerol content, or other issues will not be discussed because they generally are not affected by the fatty acid profile.

Approaches To Solve the Technical Problems Associated with the Use of Biodiesel. As mentioned above, several approaches are feasible for improving the properties of biodiesel fuels for a specific purpose. These include the use of additives, the use of different alcohols to prepare the alkyl esters other than methyl, and the modification of the fatty acid composition, including genetic modification. The latter approach also en-

compasses the winterization method for improving the low-temperature properties of biodiesel, which removes high-melting saturated components by means of cooling cycles.[5] However, a tradeoff in this case is the increased content of unsaturated fatty esters, including polyunsaturated species, which lead to concerns regarding oxidative stability and cetane number as indicated above. While using alcohols other than methanol, for example, ethanol or 2-propanol, may have a beneficial effect on cold-flow properties, their higher price in most countries around the world makes this approach economically less

Table 5. Melting Points, Kinematic Viscosity, and Oxidative Stability of Neat Fatty Esters

ester	mp (°C)[b]	kinematic viscosity (mm^2/s)[a]			oxidative stability (h)[c]
		40 °C	0 °C	−10 °C	
methyl octanoate	−37.3 (−40)	1.20	2.31	3.04	>24
ethyl octanoate	−44.5 (−43.1)	1.32	2.68	3.46	>24
methyl decanoate	−13.1 (−18)	1.71[c]	4.04[c]	4.04	>24
ethyl decanoate	−19.8 (−20)	1.87	4.28	4.28	>24
methyl laurate	4.6 (5.2)	2.43[c]	solid		>24
methyl myristoleate	−52.2	2.73[c]	7.01[c]	9.92	nd
ethyl myristoleate	−64.9	nd	nd	nd	nd
methyl palmitate	(30)	4.38[c]	solid		>24
methyl palmitoleate	−33.9	3.67	10.15	14.77	2.11 (0.11)[c]
ethyl palmitoleate	−36.6	nd	nd	nd	nd
methyl stearate	(39)	5.85	solid		>24
methyl oleate	−19.5 (−19.9)	4.51	14.03	21.33	2.79 (0.21)[c]
ethyl oleate	−20.06	4.73	14.49	22.18	2.68 (0.18)
methyl ricinoleate[d]	−5.85	15.29[c]	123.83[c]	182.36	0.67 (0.02)
methyl linoleate	(−35)	3.65	9.84	14.10	0.94 (0.10)
methyl linolenate	(−52)	3.14	7.33	10.19	0.00 (0.00)

[a] Most kinematic viscosity values are from refs 14 and 15, with some additional values determined in the course of this work. [b] Melting points are in parentheses from ref 12 or 13. For the sake of comparison and verification, some values are determined in the course of this work although given in the literature. [c] Oxidative stability per Rancimat test (EN 14112). Triplicate runs (standard deviations given in parentheses). Ethyl linoleate = 0.98 (0.09) h. [d] The viscosity determination of methyl ricinoleate at −10 °C is below its melting point because its freezing point is well below its melting point. Thus, upon cooling, methyl ricinoleate is still in the liquid phase at −10 °C.

attractive besides likely requiring changes to the transesterification reaction. Additives have the potential for improving properties, such as some cold-flow parameters or oxidative stability, but each additive affects only one property, so that several different kinds of additives may be needed. This also raises the questions of additive compatibility, effect of additives on other fuel properties, and related issues. It was reported recently that diesel particulate filter additives and to a lesser extent some cold-flow-improving additives negatively affect the oxidative stability of biodiesel.[18]

Another approach is to inherently modify the fatty acid profile of the biodiesel fuel, i.e., use a feedstock for biodiesel production that already possesses a fatty acid profile suitable for use of the resulting alkyl (usually methyl) esters as biodiesel. Such an approach has been discussed with enrichment of oleic acid in the fatty acid profile of the soybean oil feedstock.[9,10] On the other hand, some vegetable oils are inherently enriched in one fatty acid. An example is castor oil, which contains more than 85% ricinoleic acid (12-hydroxy-9(Z)-octadecenoic acid) and is increasingly used in Brazil. Methyl ricinoleate, the methyl ester of ricinoleic acid, is discussed briefly below in this work regarding its fuel properties.

The following text briefly summarizes the aforementioned fuel properties influenced by the fatty acid profile of biodiesel and then discusses possibilities for simultaneously improving these properties.

Cetane Number and Exhaust Emissions. The cetane number (CN) is a dimensionless descriptor related to the ignition quality of a fuel in a diesel engine. Generally, the higher the cetane number, the better the ignition quality of the fuel and vice versa. The CN of an individual compound depends upon the structure of the compound.[4,16] Thus, the CN of a mixture depends upon the nature of the compounds comprising the mixture. The CN increases with an increasing chain length and increasing saturation. Branched and aromatic compounds have low CNs. Thus, compounds found in biodiesel, such as methyl palmitate and methyl stearate, have high CNs, while methyl linolenate has a very low CN (see Table 4).

The CN is usually determined in an engine specifically modified for cetane testing. For example, the ASTM petrodiesel and biodiesel standards prescribe the use of ASTM D613, which uses such an engine. An alternative is the ignition quality tester (IQT), which uses significantly less material and is competitive in terms of reproducibility and repeatability. The IQT has also been established as an ASTM standard (D6890), is accepted in the ATSM biodiesel standard D6751 as an alternative to D613, and was used here.

Exhaust emissions can be at least partially related to CN. For example, nitrogen oxide (NO_x) exhaust emissions decrease to a certain extent with increasing CN, i.e., with increasing saturation of the fatty ester chain.[19] Individual components of biodiesel fuels have been compared in the literature to petrodiesel[17,20] and individual components (alkanes) of ultralow sulfur petrodiesel fuels.[17] In tests conducted in a 2003 model year heavy-duty diesel engine (comparison data given in Table 4), NO_x exhaust emissions increased slightly for methyl soyate (methyl esters of soybean oil) and technical-grade methyl oleate compared to the petrodiesel reference fuel but were slightly reduced for methyl palmitate and methyl laurate, with no chain-length dependence being observed.[17] Particulate matter (PM) exhaust emissions were reduced for all fatty materials, however, the greatest reductions were found for methyl laurate and methyl palmitate, again with slight or no chain length dependence and almost meeting 2007 Environmental Protection Agency (EPA) PM exhaust emission regulations without exhaust after-treatment technologies. All fatty compounds reduced PM exhaust emissions significantly more than hexadecane and dodecane, which would be prime components of "ultra-clean" petrodiesel fuels.[17] Methyl soyate reduced PM somewhat more than technical-grade methyl oleate. Carbon monoxide (CO) emissions were most reduced with methyl oleate and increased with a decreasing chain length for methyl laurate and methyl palmitate, an effect also observed for dodecane and hexadecane. Hydrocarbon (HC)

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exhaust emissions also increase with a decreasing chain length, with the effect even stronger than for CO. The results make it possible to qualitatively extrapolate the exhaust emissions to be expected from fuel compositions not yet tested.

Heat of Combustion. The heat of combustion or heating value is not specified in the biodiesel standards ASTM D6751 and EN14214. However, a European standard for using biodiesel as heating oil, EN 14213, specifies a minimum heating value of 35 MJ/kg. The heat of combustion increases with an increasing chain length and decreases with an increasing unsaturation (Table 4). Heats of combustion were obtained and recalculated from data given in refs 12 and 21. While differences in the heat of combustion are greatest on a molecular basis, these differences are considerably smaller on a mass basis. Accordingly, both kinds of values are given for some esters in Table 4. The heat of combustion is important for estimating fuel consumption: the greater the heat of combustion, the lower the fuel consumption. Thus, the short-chain saturated compound studied here shows the lowest heat of combustion but likely greater fuel consumption. For the sake of comparison, heat of combustion values for some alkanes as they are found in petrodiesel are 8087.1 kJ/mol and 47476 kJ/kg for dodecane and 10699.17 kJ/mol and 47475 kJ/kg for hexadecane (calculated from data in ref 12).

Low-Temperature Properties. Melting points of fatty esters generally increase with an increasing number of CH_2 moieties and decrease with an increasing unsaturation (see Table 5). While the melting point is the parameter used to assess the suitability of individual fatty esters regarding the low-temperature properties of biodiesel, parameters such as cloud point (CP), pour point (PP), and cold-filter plugging point (CFPP) are use for assessing low-temperature properties of biodiesel. However, CP, PP, and CFPP apply only to mixtures such as biodiesel. The CP is the temperature at which the first solids become visible when cooling a diesel fuel; the PP is the temperature at which the fuel ceases to flow; and the CFPP is a filterability test for cooled fuels already containing some solids. Because neat materials were investigated here, the melting point was used here. It should also be noted that the CP or other cold-flow parameter of a biodiesel fuel is determined by the amount of higher melting saturated esters or other higher melting minor components regardless of the nature of the unsaturated esters.[22]

Kinematic Viscosity. Viscosity is the major reason why fats and oils are transesterified to biodiesel. The viscosity of biodiesel is approximately an order of magnitude lower than that of the parent oil or fat, leading to better atomization of the fuel in the combustion chamber of the engine. Generally, viscosity increases with the number of CH_2 moieties in the fatty ester chain and decreases with an increasing unsaturation, with the kinematic viscosity values of a variety of fatty esters having been reported (refs 14 and 15; see Table 5). Viscosity increases exponentially with a decreasing temperature, influencing flow properties (for example, from the fuel tank to the engine), and renders this an important parameter to consider when using a fuel, such as biodiesel, at low temperatures.

Oxidative Stability. Saturated fatty esters are very oxidatively stable, while double bonds impart to fatty acids the susceptibility to reaction with oxygen. Especially, fatty acid chains with methylene-interrupted double bonds (linoleic and linolenic acids) are susceptible to oxidation. Thus, if methyl oleate is assigned

a relative oxidative rate of 1, then methyl linoleate and methyl linolenate exhibit relative oxidation rates of 41 and 98, respectively (ref 23 and references therein). The use of anti-oxidant additives is common to improve the oxidative stability of biodiesel.

The data on oxidative stability (Table 5) show that any biodiesel fuel based on unsaturated esters requires an antioxidant to meet the requirements of the ASTM D6751 and EN 14214 standards (Table 1), because even the most oxidatively stable monounsaturated fatty ester, methyl oleate, meets neither the ASTM nor EN oxidative stability specifications in the neat form.

Oxidative stability is usually assessed by the so-called Rancimat method (EN 14112) or the oil stability index (OSI) method (AOCS Cd12b-92); however, the Rancimat test is the one currently prescribed in both the ASTM and EN biodiesel standards. These tests are virtually identical. Both tests use the same principle, namely, measuring induction of an aqueous solution taking up volatile decomposition products of the sample. It must be mentioned, however, that both methods are based on using a specific mass (not moles) of sample (3 g for the Rancimat method and 5 g for the OSI method), so that, when the level of unsaturation is identical, higher molecular-weight compounds will exhibit increased oxidative stability because of their lower level of "concentration" of double bonds. Note that no data on oxidative stability is included in Table 3 regarding vegetable oil esters because in many cases in the literature it is not clear if the investigated samples contained antioxidants or not.

Lubricity. In terms of lubricity, for which the acceptable maximum wear scar values for petrodiesel fuels by the high-frequency reciprocating rig (HFRR) lubricity test are 460 and 520 μm in the European and U.S. petrodiesel standards, respectively, the nature of the fatty acid chain plays little to no role in meeting these values, although unsaturated esters possess a slight advantage.[24]

Methyl Oleate. As mentioned above, methyl oleate has been suggested in the past as a compound for enrichment in biodiesel fuels for improving biodiesel fuel properties.[9,10] The data in Tables 4 and 5 show that oleic acid is indeed a relatively suitable fatty acid for enrichment in a fatty acid profile. The enrichment of methyl oleate in vegetable oils is usually at what can be termed a technical-grade level, namely, 60–90%. The melting point of methyl oleate at −20 °C would suffice for most cold-climate conditions; however, for extreme conditions, even better performance, i.e., an even lower melting point would be preferable. The kinematic viscosity of methyl oleate increases from 4.51 mm²/s at 40 °C to 21.33 mm²/s at −10 °C, with the latter value approaching the kinematic viscosity of some vegetable oils at 40 °C. The oxidation stability of less than 3 h (per Rancimat test at 110 °C) of methyl oleate does not meet either the ASTM or EN standards. Thus, the oxidative stability of methyl oleate is considerably greater than that of the polyunsaturated esters methyl linoleate and methyl linolenate but an additive is still required for this material to meet the specifications in biodiesel standards. The cetane number of methyl oleate exceeds the minimum given in biodiesel standards (51 in EN 14214 and 47 in ASTM D6751) while possessing a low melting point. Exhaust emission tests in a newer technology engine[17] have shown that technical-grade methyl oleate (about 77%) produces slightly less NO_x exhaust emissions than commercial biodiesel but still slightly above the petrodiesel fuel

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(24) Knothe, G.; Steidley, K. R. Lubricity of components of biodiesel and petrodiesel. The origin of biodiesel lubricity. *Energy Fuels* **2005**, *19*, 1192–1200.
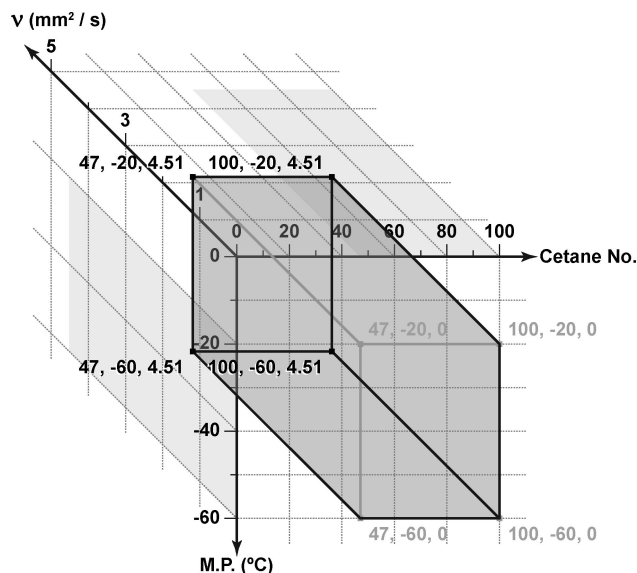
Figure 1. Plot of the cetane number for the minimum value prescribed in ASTM D6751 and kinematic viscosity (40 °C, mm²/s), as well as melting point for values of methyl oleate. Any compound whose data points are located within the shaded box would perform as well or better than methyl oleate regarding these properties.

used as base fuel. Of all biodiesel-related fuels tested (besides technical-grade methyl oleate and commercial biodiesel, also neat methyl palmitate and neat methyl laurate were investigated), technical-grade methyl oleate reduced regulated hydrocarbon and CO emissions the most. The reduction in particulate matter through the use of technical-grade methyl oleate was the least of all esters tested but still significantly greater than that of alkanes, which would be major components of "ultra-clean" petrodiesel fuels.

For purposes of visualization, Figure 1 is a three-dimensional plot of the cetane number, melting point, and kinematic viscosity. Minimum requirements for these properties are given in Figure 1 as defined by a cetane number of 47 (the minimum requirement in ASTM D6751), kinematic viscosity of 4.51 mm²/s at 40 °C (the kinematic viscosity of methyl oleate), and −20 °C (the melting point of methyl oleate). It is assumed that the oxidative stability of other suitable compounds is comparable to or better than that of methyl oleate. The data points of the neat fatty compounds that would meet these requirements are contained in the shaded rectangular box arising from the minimum requirements. Note that a minimum cetane number of 51 (as required in the European biodiesel standard EN 14214) would also be acceptable for this figure and would lead to a slightly smaller box.

The question that arises and which is dealt with in the following text, especially as a result of the cold-flow and oxidation stability properties, is if other compounds may possess some advantages regarding one or more of these properties compared to methyl oleate.

Alternatives to Methyl Oleate. The following text discusses the options for methyl palmitoleate (more generally expressed, monounsaturated esters with fatty acid chains shorter than oleate), saturated short-chain esters, esters containing hydroxy groups, and esters other than methyl. Also addressed is the issue of one-component fuels versus enriched (i.e., multicomponent) fuels.

Methyl Palmitoleate (Monounsaturated Esters with Fatty Acid Chains Shorter than Oleate). Palmitoleic acid occurs in small amounts in various vegetable oils, animal fats, and fish oils.[13] The data in Tables 4 and 5 show that methyl palmitoleate

(methyl 9(Z)-hexadecenoate) may be such an ester, although the abundance of palmitoleic acid in nature is considerably less than that of oleic acid. The cetane number of methyl palmitoleate in the tests cited in Table 4 was 51 and 56.6, meeting both the EN 14214 and ASTM D6751 specifications. However, it offers advantages in terms of kinematic viscosity: especially, the difference at low temperatures may prove to be significant. Because of its shorter chain length, the melting point of methyl palmitoleate is −33.9 °C as determined during the course of this work, about 14 °C below that of methyl oleate. Thus, methyl palmitoleate is more suitable for low-temperature applications than methyl oleate. The oxidative stability is slightly reduced compared to methyl oleate, which is likely a result of the test procedure based on mass and not on molecular weight, as discussed above.

Extrapolation of exhaust emissions for methyl palmitoleate suggests that, in comparison to the reference fuel used in the literature (ref 17; see also Table 4), NOₓ exhaust emissions are slightly increased (ca. 6%), PM emissions are significantly reduced (ca. −70%), CO emissions are significantly reduced (from ca. −40 to −50%), and HC emissions are significantly reduced (ca. 30–50%), although hydrocarbon species are the most difficult to predict.

Because of their even better cold-flow properties, esters of myristoleic (9(Z)-tetradecenoic) acid may be of interest. Some data are given in Tables 4 and 5, but the acquisition of more data was restricted because of the high price of these esters in the neat form. It may be assumed that myristoleic esters may not meet cetane number specifications because of their shorter fatty acid chains.

For the sake of completeness, it may be noted that monounsaturated esters longer than C18 are not an option because of their higher melting points. Thus, various positional isomers of *cis*-eicosenoic acid methyl esters exhibit melting points between approximately −8 and 9 °C.

Saturated Short-Chain Esters. It has been suggested anecdotally by some researchers that saturated short-chain esters may be suited for biodiesel. However, inspection of the data in Tables 4 and 5 reveals that only C_{10} esters are of interest. The major issue here again is low-temperature properties and cetane numbers. The esters of lauric acid possess too high melting points, while the esters of octanoic acid exhibit too low cetane numbers. Thus, esters of decanoic acid appear to be the most suitable saturated shorter-chain esters; however, the melting point of methyl decanoate is still significantly higher than that of methyl palmitoleate. Extrapolation of exhaust emissions for methyl decanoate using the results (ref 17; Table 4) discussed above suggests that NOₓ emissions are slightly reduced (ca. −5%) compared to the petrodiesel reference fuel, PM emissions are significantly reduced (from ca. −80 to −85%), CO emissions are reduced (from ca. −10 to −15%), and HC emissions are increased (ca. 50%). Thus, methyl oleate and methyl palmitoleate have advantages in terms of regulated exhaust emissions when considering all regulated species.

The heat of combustion of methyl decanoate is around 36 673 kJ/kg according to the data discussed above. Thus, one of the disadvantages of this material as fuel is likely somewhat higher fuel consumption compared to methyl oleate or methyl palmitoleate.

Fatty acids with an even number of carbon atoms in the chain are the most common ones in nature and are the ones that would likely be enriched in any modified oil. However, for the sake of completeness, the melting points and kinematic viscosity values of the odd-numbered fatty acid methyl esters next to C_{10},

methyl nonanoate and methyl undecanoate, were also determined. Methyl nonanoate has a melting point of −34.65 °C, and methyl undecanoate exhibits a melting point of −12 °C. The cetane number of methyl nonanoate, which was not determined, is likely slightly below the ATSM minimum of 47, as can be calculated by interpolation of the values of methyl decanoate and methyl octanoate. The cetane number of methyl undecanoate likely exceeds the minimum values prescribed in biodiesel standards, as determined by interpolation of the values of methyl decanoate and methyl laurate. The heat of combustion is not a major issue when selecting the fatty esters most suitable for biodiesel. The data in Table 4 show that the heat of combustion is in a relatively narrow range between approximately 36 600 and 40 300 kJ/kg for compounds ranging from methyl decanoate to ethyl oleate. However, methyl octanoate would not meet the European biodiesel heating oil standard EN 14213.

Esters Containing Hydroxy Groups. The hydroxy group in ricinoleic acid imparts unique properties to castor oil, the vegetable oil in which ricinoleic acid is primarily found. The high viscosity of the methyl ester of ricinoleic acid (Table 5), which exceeds the maximum values for kinematic viscosity in both the ASTM and EN biodiesel standards (Table 1) precludes the use of neat castor oil as biodiesel. At low temperatures, the viscosity of methyl ricinoleate and thus castor oil-based biodiesel is extremely high (Table 5), besides the melting point of methyl ricinoleate being relatively close to 0 °C. Furthermore, likely because of the branching imparted by the hydroxy group, the cetane number of methyl ricinoleate (Table 4) and therefore neat castor oil-based biodiesel, does not meet the minimum ASTM and EN requirements for this specification. The oxidative stability of methyl ricinoleate is significantly less than that of its nonhydroxylated counterpart methyl oleate and even reduced compared to methyl linoleate (Table 4). Therefore, methyl ricinoleate and likely hydroxy-containing fatty esters in general are not an option for enrichment in optimized biodiesel fuel formulations.

Esters Other than Methyl. Modifying the alcohol moiety is another possibility for inherently improving the fuel properties of biodiesel.[3] Ethyl esters are the most likely esters other than methyl to possess some commercial significance and are the most common form of biodiesel in Brazil. Therefore, several ethyl esters were also examined during the course of this work, as already mentioned above. Data for these esters are also included in Tables 4 and 5. The ethyl esters have slightly lower melting points than the methyl esters, with the difference in melting points increasing with a decreasing chain length. The viscosity of ethyl esters is slightly higher than that of methyl esters. The CN of ethyl esters is also slightly greater than that of methyl esters. The additional CH_2 unit in ethyl esters causes ethyl esters to have slightly higher heats of combustion than methyl esters. *Iso*-propyl esters have even better low-temperature properties than ethyl esters[3] but were not investigated in detail here.

For the sake of completeness, it may be noted that compounds with *trans* double bonds are not suitable components for biodiesel fuels. The melting point of *trans* compounds are significantly higher than those of the corresponding *cis* com-

pounds (for example, the melting point of elaidic acid, the *trans* isomer of methyl oleate, is 45 °C versus 15 °C for oleic aid), and the kinematic viscosity of monounsaturated *trans* compounds is similar to that of saturated esters of the same chain length.[14]

Multicomponent versus One-Component Fuels. Bringe[9] discussed the necessity of a mixture because of the different uses of vegetable oils, so that for physiological (nutritional) applications a favorable flavor is retained. The favorable flavor is imparted by the presence of linoleic and linolenic acids (C18:2 and C18:3).

When considering feedstocks with a fatty acid composition modified to enhance the use of the corresponding alkyl esters as fuel, several other issues need to be considered. One issue is if the modified oil can be used for other purposes. Because the major use of vegetable oils remains nutritional applications, it would need to be considered if the modified composition affects nutritional value or organoleptic properties, such as flavor and mouthfeel.[9] How the modified composition would affect economics, from development by genetic modification to growing and processing of the feedstock, would also need to be evaluated, especially because fatty acids, such as palmitoleic and decanoic acids, giving optimized fuel properties occur less commonly in vegetable oils. Another possibility is that modified fatty ester compositions with optimized properties may be developed from nontraditional feedstocks and how this would affect economics. A third issue is which fatty acids would constitute the remaining fatty acid profile of the modified oil and what their amounts would be. While enriching the oil as much as possible in one of the desirable fatty acids, small amounts of other fatty acids complete the fatty acid profile. However, the small amounts of these esters may have significant impact on the properties of the resulting biodiesel fuel. Mixtures of esters with advantageous properties, such as esters of decanoic, palmitoleic, and oleic acids, are also acceptable, if minor components with problematic properties are kept to a minimum.

Summary and Conclusions

Several approaches exist for improving the properties of biodiesel fuels by modifying fuel composition. The use of esters other than methanol and physical procedures, such as winterization, improve cold flow, with economics being an issue when using other alcohols and reduced oxidative stability and cetane numbers being issues in the case of winterization. Inherent genetic modification of the fatty acid profile offers the best possibility of addressing several or all fuel property issues simultaneously. For biodiesel, methyl palmitoleate and esters of decanoic acid are strong candidates for improving fuel properties besides methyl oleate. However, several other issues likely need to be evaluated when considering such modified feedstocks and fuels.